One step preparation of copper–silver self-catalyzed hybrid conductive ink with reduced sintering temperature for flexible electronics

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Abstract

Copper-silver hybrid conductive inks can combine the advantages of lower cost, better conductivity and long-term stability of the copper or silver ink, which have attracted wide research interest in the development of materials for flexible electronics. Although Cu-Ag nanoparticle based inks, such as Cu-Ag core-shell nanoparticle inks and Cu-Ag bimetallic nanoparticle inks, have already been developed and applied to produce conductive patterns using different deposition methods, they are still not ideal because of the complex and time-consuming synthetic process, low yield and high sintering temperature for good conductivity. In this paper, we report synthesis and characterization of novel self-catalyzed Cu-Ag organic complex inks with reduced sintering temperature via a simple one-step method. The effects of Cu-Ag ratio on the thermal property, stability and electrical performance of the formulated inks were investigated, where the Cu1-Ag1 ink was found to be ideal in terms of cost, conductivity and thermal behavior. The presence of silver oxalate in the copper complex ink was

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beneficial to the thermal decomposition of the Cu complex and able to decrease the sintering temperature by 30°C due to the catalytic function of silver, making it more compatible with flexible polymer substrate materials. Meanwhile, the addition of a small amount of silver oxalate could improve the conductivity of the Cu ink. The sintered Cu-Ag films showed favorable conductivity which is comparable to the value of the reported Cu-Ag nano inks but with a lower sintering temperature. The Cu1-Ag1 hybrid ink with self-catalyzing capability is a balanced choice considering the cost and conductivity.

Keywords: silver; copper; conductive ink; electrical properties; flexible electronics; film

1. Introduction

Currently silver based conductive inks have been the widely used conductive inks for inkjet printing due to their high conductivity and good stability in ambient conditions, and are under rapid development for the fabrication of electronic circuits such as conductive circuits [1], radio frequency identification tags [2], and sensors [3]. However the high cost and the low electromigration resistance of silver based inks limit their applications. Copper ink is an attractive alternative material to silver ink. Cu-based inks are relatively cheap and enable highly conductive tracks with higher electromigration resistance [4]. However, they are easily oxidized in the thermal treatment process of the ink and usually needs reduction atmosphere or other protective methods. Besides, the long-term stability of the obtained copper tracks in air is also a major problem for their practical applications.

Cu-Ag hybrid ink offers a solution for the above issues, which can strike a balance between cost, synthesis process, conductivity and long-term stability. Up to now, several types of Cu-Ag hybrid inks have been developed to produce conductive films and patterns.

Woo et al. developed a Cu-Ag conductive ink by dispersing the synthesized copper and silver nanoparticles in a mixture of methanol, 2-methoxy ethanol, and ethylene glycol, which could produce highly conductive tracks on a flexible substrate at a processing temperature range of 175 to 210°C [5]. It was found that the addition of small Ag particles could significantly improve the particle packing density by filling in the interstices between the larger copper nanoparticles, thus enhancing the conductivity of the copper film.

Chung et al. prepared Cu-Ag nano inks to fabricate highly conductive electrode pattern [6]. The combined silver/copper nanoparticles were first fabricated by an electrical wire explosion process and then were dispersed in a diethylene glycol solvent containing polymer to form the inks. The silver (25 wt%) and copper (75 wt%) films, sintered by white light flash irradiation, showed high resistance against oxidation with a low resistivity (4.06μΩ·cm).

Grouchko et al. developed a Cu-Ag core-shell nano ink [7]. The Cu-Ag core-shell nanoparticles were formed by a transmetalation reaction. It was found that coating 40 nm copper nanoparticles with a 2 nm layer of silver could prevent the oxidation of the copper core and preserves its metallic characteristic. The ink formed from these core-shell nanoparticles could be printed by an office inkjet printer and yielded a conductive and decorative patterns at a sintering temperature above 200°C. Lee et al.

also developed a Cu-Ag core-shell nano ink [8]. They investigated the oxidation stability of the Cu-Ag core-shell nanoparticles. The resistivity of the Cu-Ag core-shell conductive inks was measured to be 12.0μΩ·cm at 350°C, which is approximately seven times the bulk resistivity of Cu. The results also showed that the Cu-Ag core-shell nanoparticles have better electrical property than the Cu nanoparticles.

Kim et al. fabricated a low-temperature-sinterable ink composed of Cu-Ag bimetallic nanoparticles [9]. A tetramethylammonium hydroxide solution was used to decrease the sintering temperature of OA-capped Ag-Cu nanoparticles and to improve the suitability of the nanoink for use in the printing of electrodes. The electrical resistivity of the Ag-Cu nanoink after the ligand-exchange treatment was excellent as compared to the OA-capped Ag-Cu nanoparticles at 200 °C.

Although the Cu-Ag nanoparticle mixture inks, Cu-Ag core-shell nanoparticle inks, and the Cu-Ag bimetallic nanoparticle inks have already been created and conductive patterns have been obtained, they are still not ideal because of the complex and time-consuming synthetic process, low yield and higher sintering temperature required for good conductivity. To date, all types of Cu-Ag inks have been synthesized based on a two-step process, where the metal nanoparticles or the metal core-shell nanoparticles were first synthesized and then were used to formulate the inks. The process is complex and the copper nanoparticles are easy to aggregate in the synthesis process. Besides, the temperature for metalizing these particle-type inks are above 200 °C, which limits their use on a variety of flexible substrates.

Copper or silver complex inks have been developed with interests because of their flexibility in preparation, stability, low cost and low temperature sintering compared

with the particle-based inks. For instance, the ink of amine complexes of copper formate [10-18] or silver oxalate [19-22] has been a significant development and has several advantages. These inks, however, also have their drawbacks. Silver complex ink is expensive in cost and the silver patterns have low resistance against electromigration, while copper complex ink has poor conductivity due to the low content of copper in the organic copper precursor. This is especially true in the case of copper (II) formate tetrahydrate, where the weight fraction of copper is only 4.1 %. After formulating into the ink, the weight fraction of copper will be much lower due to the addition of solvents and complexing agent, thereby resulting in poor film quality. Therefore, it will be advantageous to develop a copper-silver hybrid complex ink combining the benefits of low cost of copper and good conductivity of silver. Recently it has been shown that it is possible to produce metal complex based Cu-Ag conductive ink when catalytic activity of silver was used to accelerate the decomposition of the copper complex into pure metal particles under mild and low-temperature conditions [23]. Inspired by this work, we formulated new Cu-Ag hybrid inks based on the simultaneous complexation reaction of Cuf and AgOX with an amine. The process is simple, facile and only one-step. The effects of Cu-Ag ratio on the thermal property, stability and electrical performance of the produced films were investigated in detail. We show that the sintering temperature of the hybrid ink can be 30 °C lower than that of the Cuf complex ink, making the hybrid ink more compatible with polymer based flexible substrates and also taking the low cost advantage of copper based inks.

2. Experimental Section

2.1 Preparation of silver-amine complex ink and film

Copper (II) formate tetrahydrate ($C_2H_{10}CuO_8$, Cuf) was purchased from Alfa Aesar. 1,2-diaminopropane ($C_3H_{10}N_2$, DAP), ethylene glycol ($C_2O_2H_6$, EG) and ethanol (C_2H_6O, EA) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Silver oxalate ($Ag_2C_2O_4$, AgOX) was synthesized using the method of our previous work [21]. Polyimide films (PI) of 127μm of thickness were obtained from DuPont. Before application, 15mm×15mm PI samples were cleaned with deionized water and ethanol.

Table 1 Ag and Cu content of each Ink

Ink No.	M_{Cuf} (g)	M_{AgOX} (g)	M_{Cu}/M_{Ag}	V_{DAP} (ml)
1	0.226	0	Cu	0.172
2	0.177	0.0141	5:1	0.151
3	0.142	0.0282	2:1	0.140
4	0.107	0.0423	1:1	0.129
5	0.071	0.0563	1:2	0.118
6	0.036	0.0704	1:5	0.107
7	0	0.152	Ag	0.172

Copper-silver organic hybrid inks were prepared through a complexation process of Cuf, AgOX and DAP at room temperature. The Cuf and AgOX with different weight ratios were first dispersed in a solution containing ethanol (0.375 ml) and ethylene glycol (0.375 ml) under vigorous stirring separately. Then, a certain amount of DPA was added at once via a syringe. The mixture was stirred for 60 minutes to form each ink. The molar ratios of metal/amine were kept at a constant value of 1:2. The obtained inks were stored in a refrigerator to maintain their stability. Table 1 shows the Ag and Cu content of each ink by weight.

A drop-casting method was used to prepare the films. Two drops of each ink were deposited and spread evenly on the surface of PI substrates (15mm×15mm) by using a

disposable transfer pipettes (Thermo Scientific™ Samco™, 3.2ml). For metallization, the obtained wet films were sintered in nitrogen at selected temperatures for 60 minutes.

2.2 Characterization

Fourier transforms infrared (FT-IR) spectra of the complexes were obtained on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance diffractometer using Cu Kα radiation and λ = 0.15418 nm. Samples were scanned over a 2θrange of 5-85°. Thermal behaviors of the as-prepared inks were investigated on a thermal analyzer (TA instrument) using aluminum pans at a heating rate of 10 °C min^{-1} from room temperature to 300 °C and a nitrogen flow rate of 80 ml min^{-1}. Since Al is a good reducing agent for Cu ions. We observed the state of the aluminum pan before and after the DSC test, where no corrosion pits were generated. It has been reported that Al does not react with some types of copper salts, which might be the reason for our case [24]. Surface morphologies of the samples were observed via a FEI Quanta 3D Scanning Electron Microscope (SEM) and chemical composition was confirmed by an Oxford X-maxN 150 surface energy disperse spectrometer (EDX). The sheet resistance of the films was measured by using a four-point probe system (Jandel Engineering, UK). The thickness of the film was measured by a Dektak surface profilometer. The average thickness of each film was used to calculate the film resistivity.

3. Results and discussion

3.1 Ink formulation principle

The copper-silver organic hybrid inks were formed mainly via the following chemical process: the amino group (-NH_2) of 1,2-diaminopropane coordinates with the

silver [19] and copper atoms [10] separately, and subsequently form the metal complexes.

$$Ag_2C_2O_4 + 2C_3H_{10}N_2 \rightarrow [Ag(C_3H_{10}N_2)]_2C_2O_4$$

$$Cu(HCOO)_2 \cdot 4H_2O + 2C_3H_{10}N_2 \rightarrow [Cu(C_3H_{10}N_2)_2](HCOO)_2 \cdot 4H_2O$$

When the metal complexes are formed, the electrons from the amino group of the ligand DAP will be donated to the Cu or Ag ions, resulting in their partial reduction [15]. Thus, it can be inferred that the ligands $C_2O_4^{2-}$ and $HCOO^-$ of the complexes are more easily released than those of the Cuf or AgOX during thermal sintering. In other words, the complex will be more easily decomposed than Cuf or AgOX.

The optical images of the freshly prepared copper complex ink, silver complex ink and hybrid complex inks with different Cu-Ag ratios are shown in Fig.1. The Cu complex ink has a deep blue color while the silver complex ink is colorless. The color of the hybrid ink becomes lighter with the increase of silver content.

To further understand the chemical states of the formulated inks and to confirm the above reaction mechanism, the organic functional groups in the Cuf, DAP, Cuf-amine complex and Cu5-Ag1-amine complex were investigated by FT-IR measurements (Fig. 2).

In the spectrum of Cuf, the peaks at 1552 and 1360 cm^{-1} are attributed to the stretching vibrations of C=O and C-O, respectively. A small peak at 2881 cm^{-1} is the stretching vibration of C-H. These bands originated from the ligand carboxyl group of Cuf. Another small peak at 833 cm^{-1} is attributed to Cu-O-H vibration, reflecting the ligand carboxyl group that forms the bond with the Cu(II) in Cuf. A broad band around 3200 cm^{-1} was assigned to the O-H bond of tetrahydrate contained in Cuf. For the DAP

spectrum, the absorption peaks appeared at 3357 and 3280 cm^{-1} were from the asymmetric and the symmetric stretch of NH_2 groups. Two peaks at 2956 and 2921 cm^{-1} were assigned to the asymmetric stretch of CH_3 and CH_2, respectively. The peak at 2863cm^{-1} is related to the symmetric stretching mode of CH_2. After complexation, the formulated Cu-Ag complex showed the characteristic features of both neat Cuf and DPA. However, the peaks associated with the NH_2 groups have a dramatic red-shift, from 3357 to 3246 cm^{-1}, and 3280 to 3146 cm^{-1}. Besides, the carboxyl group related peaks also shifted after complexation, from 1552 to 1572 cm^{-1}, indicating the dissociation of a Cu(II)-bonded carboxyl group into a free carboxyl group. All these changes indicate that 1,2-diaminopropane reacted with AgOX and Cuf, and donate electrons from the amino group to the silver or copper ion, which decreased the electron density of the amino group and causing the particle reduction of the metal ion, thus resulting in the red shift of the NH_2 and carboxyl group.

It should be mentioned that in order to eliminate the influence from the solvents, the complex for the FT-IR measurement was prepared using only AgOX, Cuf and 1,2-diaminopropane in a molar ratio of 1:2.

Here, the stability of the as-prepared inks was also evaluated. At room temperature for one day, no changes occur in all the inks. However, after 30 days, only the copper ink had no obvious change in color. When storing in a refrigerator at 3°C for 30 days, the silver ink, copper ink and the inks composed of Cu1-Ag5 or Cu1-Ag2 and Cu1-Ag1 were still transparent and no obvious color change and sediment, implying favorable stability.

3.2 Thermal behavior of copper, silver and copper-silver hybrid conductive inks

DSC analysis was used to investigate the thermal behavior of the obtained silver, copper and silver-copper hybrid complex inks, and the results are given in Fig.3a. The broad peak at a temperature below 60°C is mainly attributed to the evaporation of ethanol (ink solvent) because of its lower boiling point, while the peak in the range of 130-140°C is assigned to the decomposition of ethylene glycol based on the previous research [21, 25]. The silver complex ink displays a relatively low decomposition temperature (142°C) in comparison with that of the copper complex ink (175°C). The decomposition temperature of the copper-silver hybrid inks is between the two, where the inks composed of Cu1-Ag5 and Cu1-Ag2 show a thermal behavior similar to that of the silver complex ink. The thermal behavior of the inks composed of Cu5-Ag1 and Cu2-Ag1 is similar to that of the copper complex ink. Besides, it can be clearly seen that the decomposition temperature of the inks decreases with the increase of the weight ratio of Ag to Cu, which may be associated with the catalytic effect of silver nanoparticles in the sintering process [23]. When the two metal complexes are mixed, silver nanoparticles were formed firstly due to its lower thermal decomposition temperature, followed by the formation of copper nanoparticles. These in situ formed silver nanoparticles have good catalytic property, which can serve as catalysts to accelerate the decomposition of the Cu complex, thereby leading to a low temperature self-catalyzed decomposition process [23]. This is why the Cu-Ag hybrid inks show a decomposition temperature between those of the silver complex ink and the copper complex ink. The Cu and Ag phase are continually formed from the decomposition of the Cu-Ag complex during this self-catalyzed process, and Cu-Ag hybrid structures are produced.

The results show that the temperature of the Cu-Ag complex ink can be decreased from that of the pure Cuf-DAP complex inks, which is an advantage. Also considering the ink cost, the Cu1-Ag1 ink was selected for the subsequent experiments.

Here, the DSC results of AgOX and Cuf are also given in Fig.3b. The AgOX shows two major endothermic peaks at 166°C and 190°C, while the Cuf shows four peaks. The first three peaks are associated with the dehydration of the Cuf and the last peak at 210°C is attributed to the decomposition of Cuf. These results are consistent with that reported in Ref [15]. The decomposition temperatures of hybrid inks are much lower than that of AgOX or Cuf, indicating the positive effect of DAP as a complexing agent.

3.3 Phase composition, morphology and resistivity of the films from various inks

Based on the results of the DSC analysis, the temperature of 180°C was selected to sinter the obtained inks to investigate the influence of Cu-Ag ratio on the resistivity, physical composition and morphology of the obtained films.

Fig.4 shows the resistivity of the films obtained at 180°C for 60min from the copper ink, silver ink and Cu-Ag hybrid inks. Notably, the resistivity of each film is related to the silver content in the ink. The film from the silver ink showed the lowest resistivity of 33.6μΩ·cm, while the film derived from copper ink had a relatively high resistivity of 177.4μΩ·cm. The resistivity of the films derived from the copper-silver hybrid inks decreased with the increase of silver content. In combination with the results of DSC, it can be inferred that the evaporation of solvent and the decomposition of silver complex in all inks are complete at 180°C. The produced silver nanoparticles connected well with each other and served as the catalysts to accelerate the decomposition of copper complex, thereby leading to a decrease in the resistivity of

silver-rich inks. For copper-rich inks, the decomposition of copper complex is inadequate due to the high decomposition temperature, thereby having a relatively high resistivity.

X-ray diffraction and SEM methods were then used to determine the crystalline structure and surface microstructure of the obtained films from various complex inks (Fig.5 and Fig.6) to gain insight into the underlying reasons for various sheet resistances of films from different inks.

It can be seen that all the films produced from the hybrid inks show a clear dual-phase structure, with a preferred orientation at (111). The peak intensity of copper nanocrystals increases with the copper content. The prominent peaks at 38.2°, 44.4°, 64.5°, 77.5° and 81.6° are all in good agreement with the characteristic values for crystalline silver. The peaks at 43.2°, 50.3° and 74.1° correspond to the (111), (200) and (220) crystal planes of copper crystalline. These results indicated that the Cu-Ag hybrid complex inks were transformed into silver and copper crystals, and the following reaction occurred [22, 26].

$$[Ag(C_3H_{10}N_2)]_2C_2O_4 \xrightarrow{\Delta} 2Ag(s) + 2CO_2(g)\uparrow + 2C_3H_{10}N_2(g)\uparrow$$

$$[Cu(C_3H_{10}N_2)_2](HCOO)_2 \cdot 4H_2O \xrightarrow{\Delta} Cu(s) + 4H_2O(g)\uparrow + 2C_3H_{10}N_2(g)\uparrow + 2CO_2(g)\uparrow + H_2(g)\uparrow$$

Generally, nanoscale particles are metastable owing to higher percentages of the surface area, which makes them more readily oxidized in air. Copper nanoparitcles are easily oxidized into either Cu_2O or CuO, both of which are less conductive. However,

no diffraction peaks from Cu_2O or CuO were detected, indicating that the produced films have a certain degree of anti-oxidation stability.

According to the work by Dong et al., the anti-oxidation behavior of diamine inks is related to the formation of imine during sintering [26]. Diamines can react with molecular O_2 to form imine, and thus prevent the as-formed Cu film from oxidation by isolating oxygen. Besides, in our case, a beneficial nitrogen atmosphere was employed during the film sintering process. Therefore, no Cu_2O or CuO is detected in our XRD spectra.

Fig.6 shows the SEM images of the films produced from seven metal complex inks. It can be seen that the films have diverse morphologies. The film derived from the copper complex ink showed a surface structure consisting of near-spherical copper nanoparticles (Fig.6a), while the silver film from the silver complex ink, showed a structure consisting of silver nanoparticles that have good connection between the particles (Fig.6j and j_1). The films produced from the Cu5-Ag1 and Cu2-Ag1 complex inks show a surface structure composed of near-spherical particles and aggregated particles with irregular morphology, where the latter covers the surface of the former. The films from the Cu1-Ag1 and Cu1-Ag2 complex inks displayed a loose surface morphology that was composed of big particles and more voids. The silver films from Cu1-Ag5 ink had a structure that was composed of fused particles, free near-spherical particles and few voids.

The influences of Cu-Ag weight ratio on the microstructure morphology of the yield films from different complex inks during sintering process are analyzed as follows. For the Cu5-Ag1 and Cu2-Ag1 complex inks, during the sintering, the silver complex in

the over-saturated Cu-rich ink firstly decomposed to silver owing to their lower decomposition temperature. These silver particles, however, were separated by the liquid copper complex and could not agglomerate quickly until the decomposition of the copper complex. Since the unreacted liquid copper complex can produce a strong capillary force pulling the particles into close contact, therefore the film shows a hierarchical structure, where the agglormated particles covered a uniform surface composed of near-spherical particles. With the increase of silver content in the inks (Cu1-Ag1, Cu1-Ag2 and Cu1-Ag5), Cu particles can be fully covered by silver. Hence, the films display a surface morphology similar to that from silver ink but have more voids.

The EDX point energy spectra were obtained to identify the chemical composition of the aggregated particles and the small spheroid-like particles in the films derived from Cu5-Ag1 ink (Fig. 7a and 7b, respectively). The samples were taken from the area 1 and 2 in Fig.6b. From the results, it can be seen that the aggregated particles and the small spheroid-like particles both are not the sole silver or copper particles but the mixtures of the two. The EDX surface energy spectrum of the film produced from Cu1-Ag1 ink was also given (Fig.7c and d). Four elements (C, O, Cu and Ag) were detected, where the mass ratio of copper to silver is about 1:1. This is in accordance with the formulation design of the ink. The distribution of silver and copper nanoparticles in the film was analyzed by the EDX mapping method, as shown in Fig.7d_1 and d_2. The elements of Cu and Ag were uniformly distributed and overlapped, proving the previous assumption. This result indicated that the formation of Cu-Ag structure is a result of nucleation and growth of Cu and Ag, where they are mutually dependent on each other.

Since the silver complex has a lower decomposition temperature, silver particles are firstly generated, which can serve as a catalyst to prompt the decomposition of the copper complex. These silver particles are then covered by the newly formed Cu. After that, the Cu is covered by the formed Ag phase again, thereby resulting in the mixed structure composed of copper and silver.

3.4 Temperature dependence of the films from Cu1-Ag1 ink

Fig.8 shows the XRD patterns of films from the Cu1-Ag1 ink sintered at temperatures of 130, 140, 150, 160, 170 and 180°C respectively, for 60 minutes. All the films showed characteristic peaks corresponding to metal silver and copper, revealing the formation of bimetallic films. Below 150°C, the peak intensities of metal copper or silver increased gradually with the sintering temperature. After 150°C, however, the change was not obvious in both cases, indicating a well-crystallized copper-silver bimetallic film has been formed.

The crystallite sizes of the copper and silver nanoparticles in the films were calculated using the XRD data. The results are given in Table 2.

It can be seen that the crystallite sizes of the copper nanoparticles increase significantly with increasing temperature, from 39.31nm at 130°C to 49.3nm at 150°C. But after that it increases slowly. The crystallite sizes of the silver nanoparticles in the film show the same feature with that of copper. These results indicate that the nucleation of the copper or silver grains was basically completed at 150°C, and the grain growth and connection followed after this temperature.

Table 2 Particle sizes of copper and silver nanocrystals in films at different sintering temperatures

Temperature	Cu 2θ	Ag 2θ	FWHM	FWHM	Cu	Ag

(°C)	(Degrees)	(Degrees)	(Cu)	(Ag)	Size (nm)	Size (nm)
130	43.499	38.259	0.206	0.200	39.31	40.90
140	43.324	38.120	0.172	0.181	48.30	44.42
150	43.380	38.193	0.167	0.160	49.30	50.68
160	43.362	38.175	0.164	0.160	50.34	50.56
170	43.362	38.175	0.162	0.159	50.96	50.88
180	43.315	38.146	0.165	0.156	50.43	51.68

Fig.9 (a-f) was the corresponding microstructure changes. The film sintered at 130°C shows a surface structure consisting of particles embedded in organic matters. These organic matters were from the EG and unreacted copper or silver complex as they could not be thermally evaporated or decomposed completely at this temperature. The embedded particles are exposed when the temperature is increased to 150°C, corresponding to further decomposition of the complex and the EG. The films sintered at 160, 170 and 180 °C showed a microstructure with densely packed particles and few voids, indicating an enhanced sintering. Besides, sintering necks are observed between particles in the films sintered at 170 and 180 °C.

The differences in the microstructures were related to particle nucleation and growth. In our case, the decomposition of the copper and silver complexes resulting in the nucleation of particles occurred in the first stage because of the low decomposition temperature, and then the growth of the particles occurred in the remaining process.

EDX analysis was employed to investigate the changes in chemical composition; the results are shown in Fig.10. As the sintering temperature was increased from 130°C

to 180°C, obvious changes in Ag and C content were observed. This indicated that the organic molecules were decomposed or volatilized mostly and the decomposition of silver complexes was gradually completed. The change of copper content was not obvious with the temperature change, indicating that Cuf complex has been decomposed into copper mostly at 150°C. This may be related to the catalytic action of silver nanoparticles, which accelerates the decomposition of Cuf complex at this temperature. Since EDS does not differentiate between metallic metal and ionic metal, no change would expect to see in the Ag/Cu ratio at all stage. However, the Ag/Cu ratio changes slightly here. As for the reason, it may be associated with the uneven distribution of Cu and Ag nanoparticles in the film, where the area selected for EDS test has difference in different position.

The resistivity of the copper films, silver films and the bimetallic hybrid films obtained at various temperatures from the corresponding inks, was calculated from the measured sheet resistance and the film thickness (the thickness of hybrid films from Cu1-Ag1 ink is about 2.8±0.4μm), the results are shown in Fig.11. For the Ag and Cu-Ag films the resistivity decreases rapidly as the sintering temperature was increased from 130°C to 180°C. The resistivity of the Ag films decreased gradually from 632.5 μΩ·cm to 33.62 μΩ·cm, and the resistivity of Cu-Ag hybrid films decreased from 685.34μΩ·cm to 90.56μΩ·cm. Below 130 °C, the film of each case was partly wet and the resistivity was too high to be measured by the 4-probe instrument. After 130°C, the resistivity in Cu-Ag and Ag films decreased dramatically. In combination with the previous analysis, this was a consequence of the decomposition of silver complex and the catalytic effect of silver nanoparticles. When the temperature was above 150°C, the

resistivity of each film decreased slowly, where the value of hybrid film was higher than that of Ag films but lower than the copper films, indicating that the positive effect of silver in the hybrid ink. According to the formulation of Cu1-Ag1 ink, the weight fraction of metal silver was only 3.0% and the same value for metal copper. This is the reason why the conductivity of the Cu-Ag film was not as good as that of the silver complex ink, where the weight fraction of silver was about 10%.

The decrease in resistivity with temperature can be explained by the fact that the evaporation of solvent was adequate, and more copper or silver particles or both were generated, became larger, and had a close connection between each other.

The storage stability of the Cu/Ag hybrid films obtained at 180°C from Cu1-Ag1 ink was also evaluated. After storing at the room temperature for 6 months, the resistivity of the film was measured to be 93.52μΩ·cm, which a slight increase from that of 90.56μΩ·cm, indicating that the films have good stability.

The resistivity at 180°C was around 10^{-5}Ω·cm, which was comparable to the value of the reported Cu-Ag nano inks but with a lower sintering temperature, making the ink more compatible with flexible polymer substrates. Besides, the synthesis method of our hybrid inks was much simple, only one step. The formulated Cu-Ag ink not only decreases the cost of the Ag ink but also improves the conductivity of the copper ink at a low sintering temperature. This shows the advantage of the Ag-Cu hybrid inks.

4. Conclusions

In summary Cu/Ag hybrid inks with low-temperature sintering capability were synthesized by a one-step method. The effects of Cu-Ag ratio on the thermal property, stability and electrical performance of the inks were investigated, where the Cu1-Ag1

ink was the best in terms of cost, conductivity and thermal behavior. The addition of silver oxalate in the copper complex ink can significantly affect the decomposition behavior of the Cuf complex and decrease the sintering temperature by 30°C. The Cu-Ag films from the Cu1-Ag1 ink showed favorable conductivity at a low sintering temperature compared to Cuf complex. Further development of the work may lead to metal hybrid conductive inks for future wearable and consumer electronics.

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Notes

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Figures Captions

Fig.1. Optical images of the as-prepared copper ink, silver ink and hybrid inks with different Cu-Ag ratios

Fig.2. FT-IR spectra of Cuf, DAP, Cu-amine complex and Cu5-Ag1-amine complex

Fig.3. a) DSC curves of the as-prepared copper ink, silver ink and Cu-Ag hybrid conductive inks; b) DSC curves of AgOX and Cuf

Fig.4. Resistivity of films sintered at 180°C for 60min from the as-prepared copper ink, silver ink and Cu-Ag hybrid conductive inks

Fig.5. XRD patterns of films sintered at 180°C for 60min from the as-prepared copper ink, silver ink and Cu-Ag hybrid conductive inks with different Cu-Ag ratios

Fig.6. SEM images of silver film, copper film and copper-silver hybrid films sintered at 180°C for 60min from the copper ink, silver ink and Cu-Ag hybrid inks, (a, a_1) Cu ink, (b, b_1) Cu5-Ag1 ink, (c, c_1) Cu2-Ag1 ink, (d, d_1) Cu1-Ag1 ink, (e, e_1) Cu1-Ag2 ink, (f) Cu1-Ag5 ink (f_1 is high magnification image of figure f), (j, j_1) Ag ink

Fig.7. EDX results of copper-silver hybrid conductive films sintered at 180°C for 60min, (a, b) point energy spectra of the particles in the film derived from the Cu5-Ag1 ink, (c, d) surface morphology image and surface energy spectrum of the film from Cu1-Ag1 ink, (d_1-d_4) EDX element mapping results

Fig.8. XRD patterns of copper-silver hybrid conductive films sintered at different temperatures for 60min from Cu1-Ag1 ink

Fig.9. SEM images of copper-silver hybrid conductive films sintered at different temperatures for 60min from Cu1-Ag1 ink, (a) 130°C, (b) 140°C, (c) 150°C, (d) 160°C, (e) 170°C and (f) 180°C (a_1-f_1 are the high magnification images of figure a-f)

Fig.10. EDX images of copper-silver hybrid conductive films sintered at different temperatures for 60min from Cu1-Ag1 ink, (a_1) 130°C, (c_1) 150°C, (d_1) 160°C and (f_1) 180°C

Fig.11. Resistivity of copper-silver hybrid conductive films sintered at different temperatures for 60min from the silver ink, copper ink and Cu1-Ag1 ink

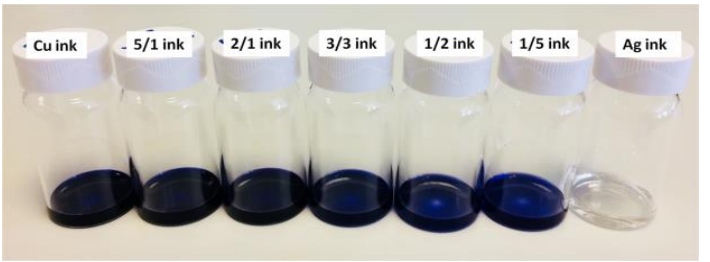
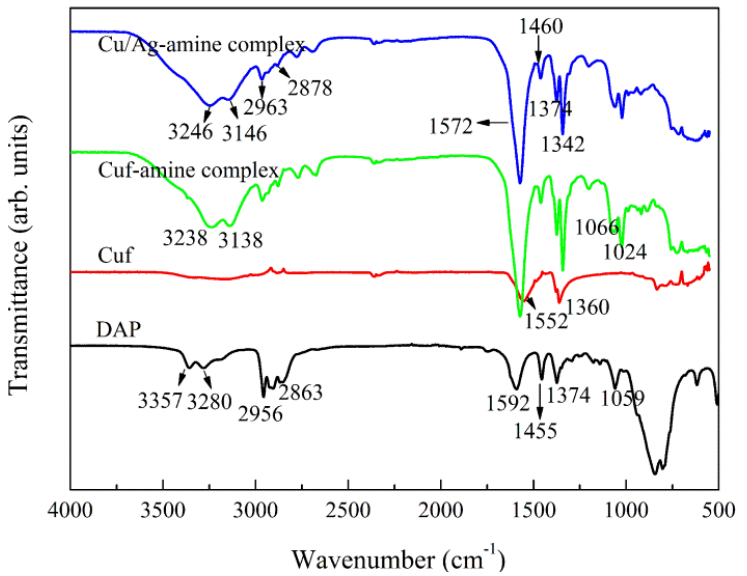


Fig.1. Optical images of the as-prepared copper ink, silver ink and hybrid inks with different Cu-Ag ratios



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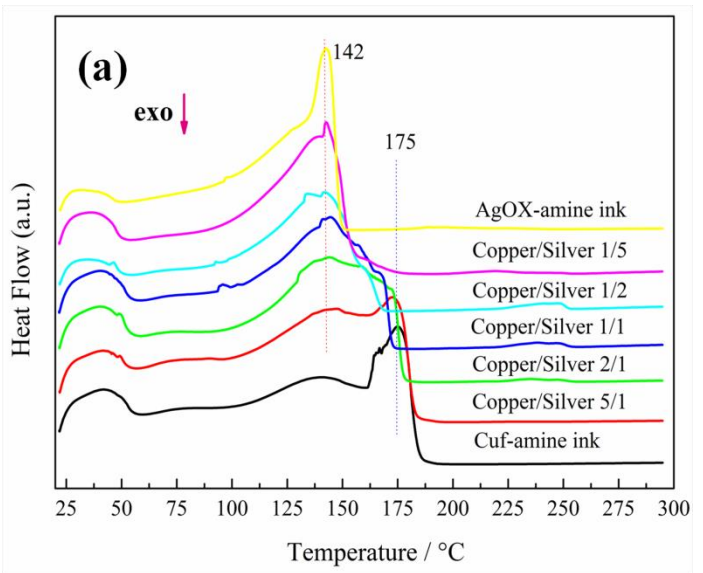

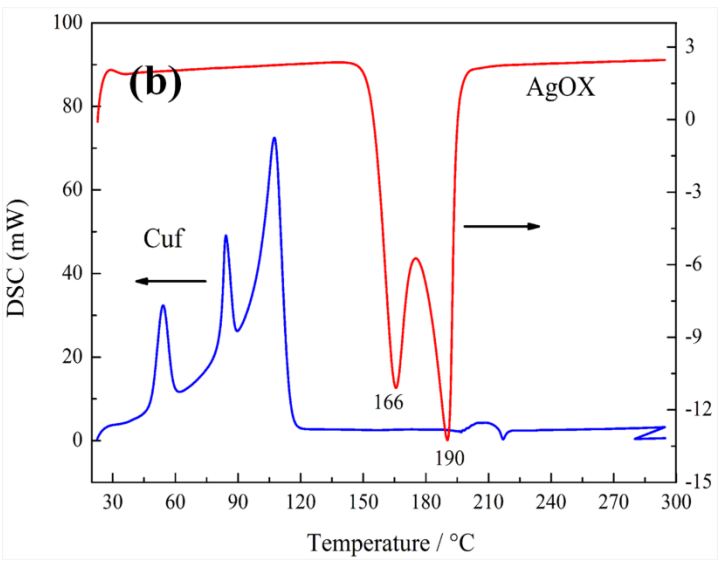

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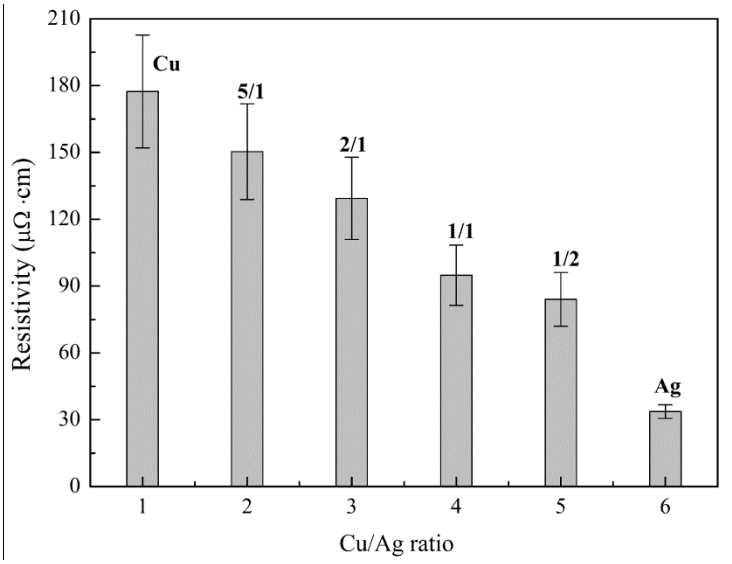


Fig.4. Resistivity of films sintered at 180°C for 60min from the as-prepared copper ink, silver ink and Cu-Ag hybrid conductive inks

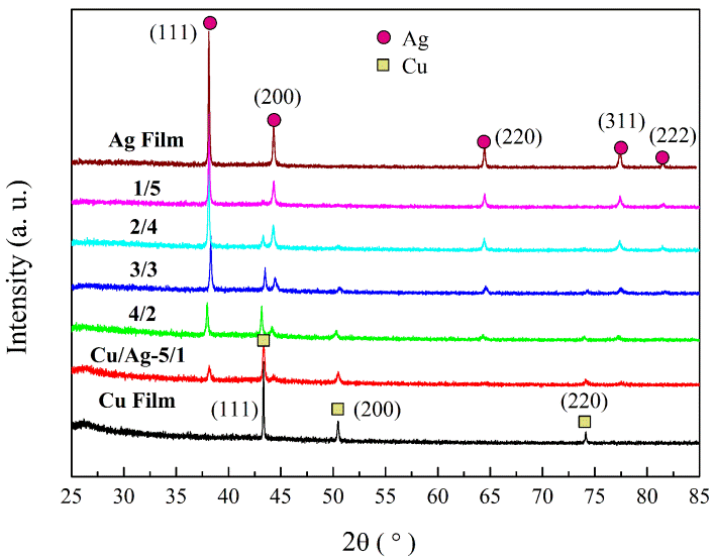
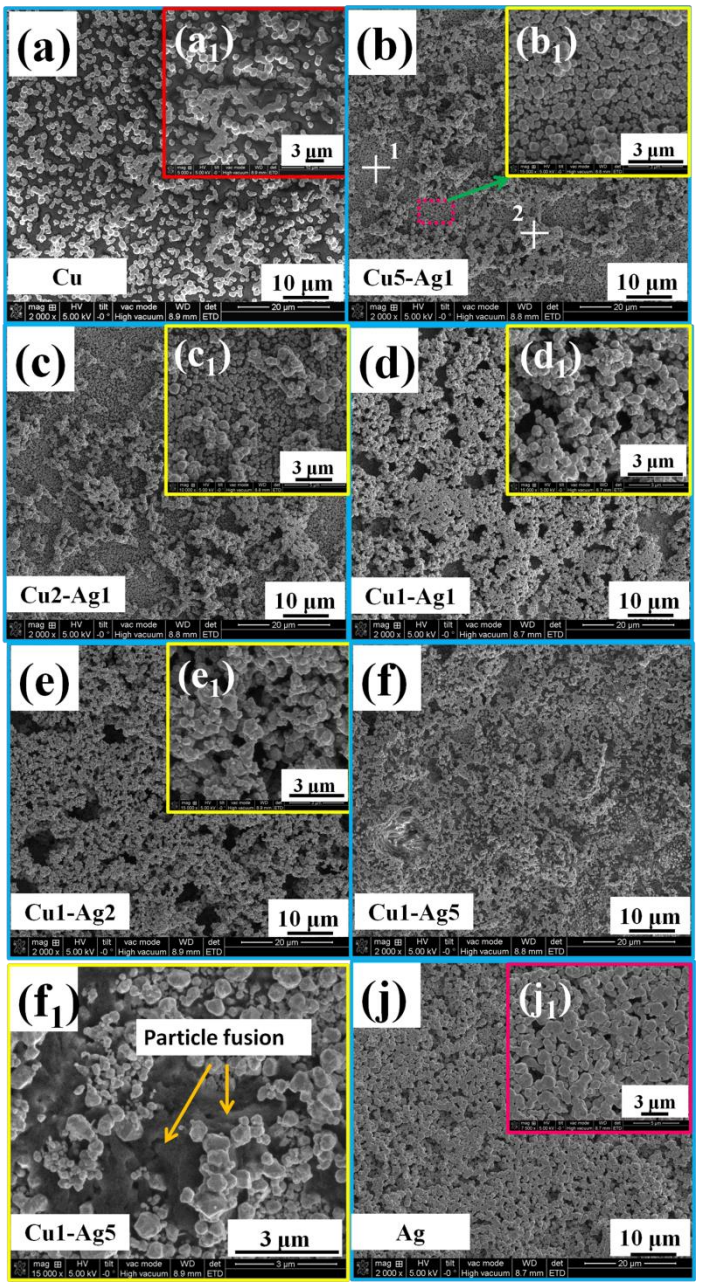


Fig.5. XRD patterns of films sintered at 180°C for 60min from the as-prepared copper ink, silver ink and Cu-Ag hybrid conductive inks with different Cu-Ag ratios



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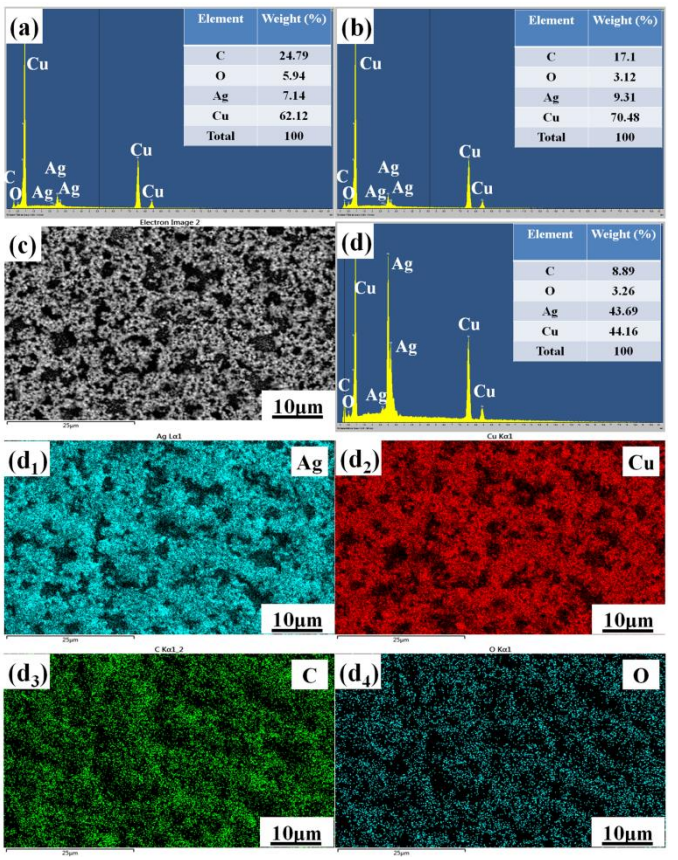
Cu1-Ag5 ink (f_1 is high magnification image of figure f), (j, j_1) Ag ink



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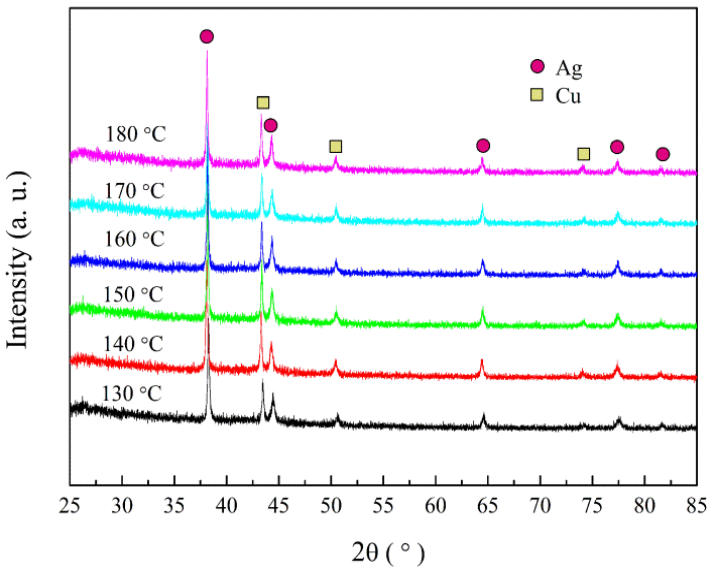
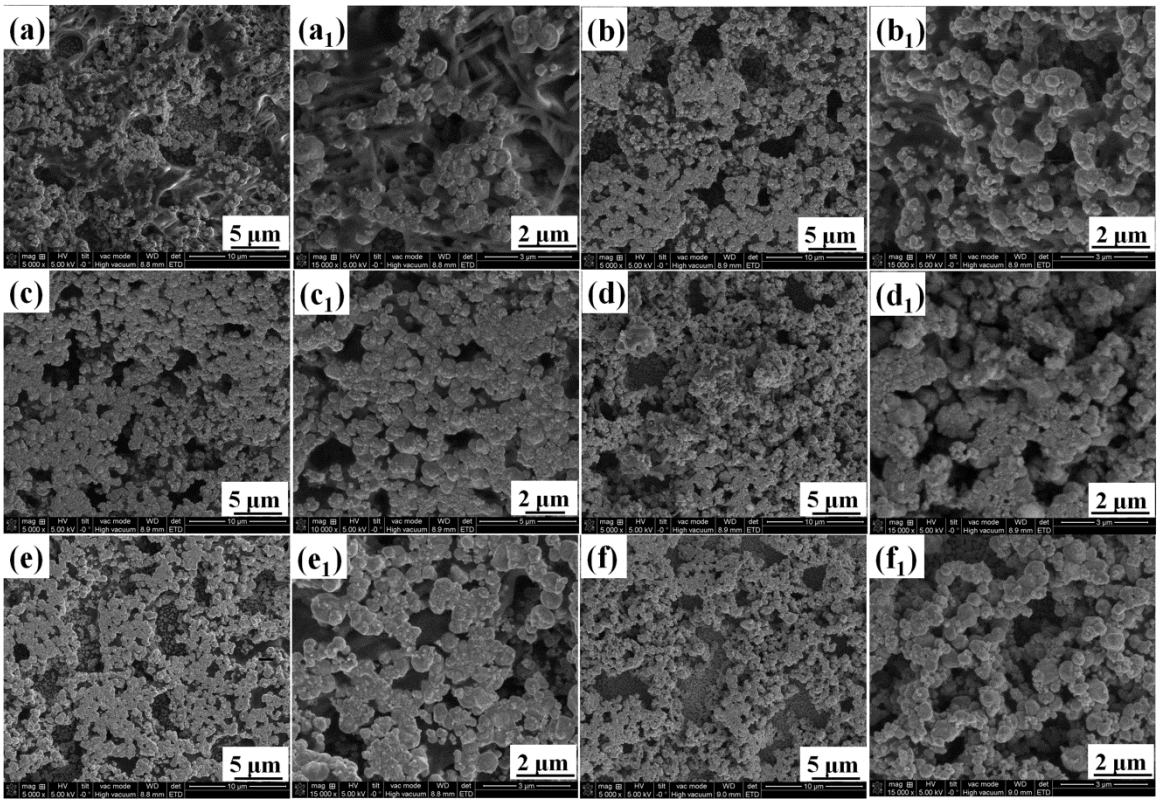


Fig.8. XRD patterns of copper-silver hybrid conductive films sintered at different temperatures for 60min from Cu1-Ag1 ink



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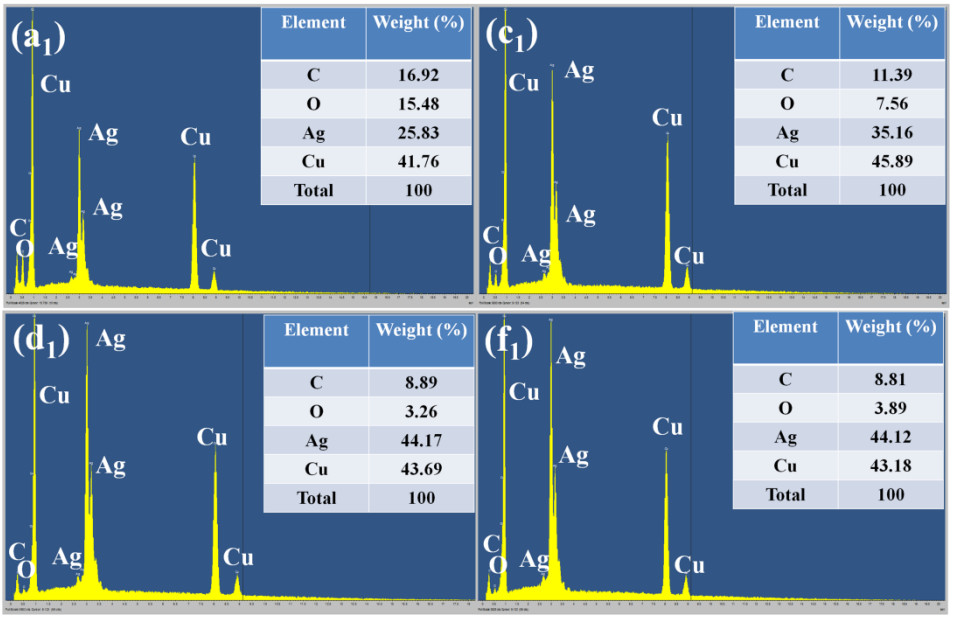

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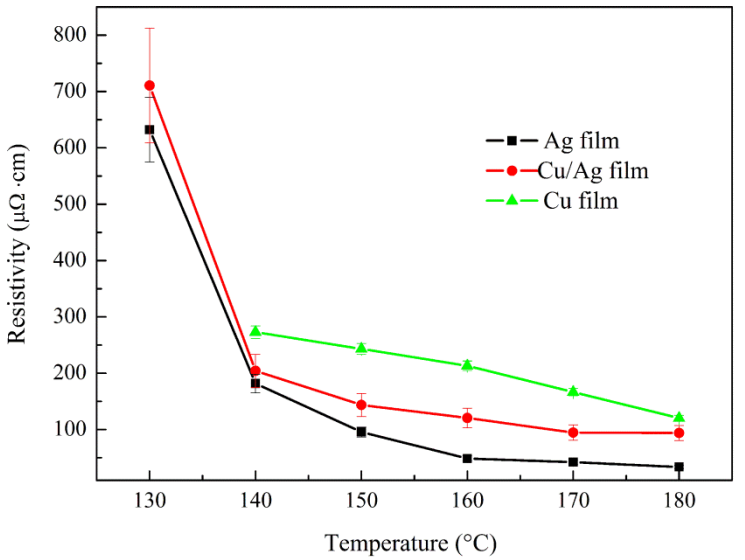

Fig.11. Resistivity of copper-silver hybrid conductive films sintered at different temperatures for 60min from the silver ink, copper ink and Cu1-Ag1 ink